ACTIVATED CARBON FIBERS AND FILMS PREPARED FROM POLY(VINYLIDENE FLUORIDE) BY USING A CHEMICAL CARBONIZATION

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1. INTRODUCTION

Activated carbons with excellent adsorptive properties have been used in many fields such as separation of mixtures and removal of contaminant impurities. The granular activated carbons have been produced mainly from palm shells and coal. As compared with the granular activated carbons, activated carbon fibers prepared from synthetic fibers have an advantage to process into various shapes such as fabrics and papers. Furthermore, high adsorption-desorption rate of activated carbon fibers is also advantageous. The activated carbon fibers produced by convential methods, however, are microporous and they are insufficient for the purpose of adsorbing large molecules.

Recently, several attempts have been made to introduce mesopores into carbons. For example, mesoporous carbons have been obtained by steam activation of the carbons derived from mixtures of pitch and metal complexes [1-3]. It is considered, however, that the metal residues in these carbons bring about unfavorable effects for the application to catalyst supports. Thus, new methods to prepare the mesoporous carbons free from metal complexes are required.

The present authors have obtained carbon fibers and films with various average pore sizes by applying a combination of dehydrofluorination and high-temperature heat-treatment to poly(vinylidene fluoride) (PVDF) [4]. In this study, PVDF-based carbons derived with this method were further activated. The porous structure and adsorptive properties of the resulting activated carbons were investigated by using nitrogen gas and methylene blue as adsobates.

2. EXPERIMENTAL

The PVDF fibers with small diameters in a range of 7-10 μm were prepared by firstly spinning bicomponent fibers which consisted 261 continuous filaments of PVDF core fibers and polystyrene matrix and secondly dissolving the matrix. The bicomponent fibers were spun using a melt-spinning technique with the spinning temperature at 290°C and the take-up velocity of 100 m min^{-1}. For dissolving the matrix, the bicomponent fibers were soaked in tetrahydrofuran at 50°C for 90 min. Then, obtained PVDF fibers were washed in methanol and dried under reduced pressure.

PVDF films with a thickness of about 120 μm were prepared by hot-pressing PVDF pellets at 200°C and quenching them between steel plates at room temperature. The films were cut into the sizes of 7.5 mm by 10 mm.

The dehydrofluorination of PVDF fibers and films were carried out by using one of the strongest organic base, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), under a swollen state. The degree of swelling was controlled by using a mixture of a swelling solvent, dimethylformamide (DMF), and a nonsolvent, ethanol (EtOH), with a volume ratio of DMF/EtOH = 2/3. The PVDF fiber bundles and films by the amounts corresponding to the number ratio of DBU/(vinylidene fluoride unit) = 4/1 were soaked in a DMF-EtOH solution of 1.0 M DBU at 70°C. During this treatment, a slight tension was applied to the fiber bundle. After the treatment, the fibers and films were washed in methanol for 1 h and

dried under reduced pressure. In the following, 'untreated PVDF' will refer to the PVDF that was not dehydrofluorinated.

The dehydrofluorinated fibers and films were heated at a rate of 2°C min^{-1} up to desired temperatures below 1300°C in a nitrogen atmosphere. During the heat-treatments, the fibers were slightly tensioned, and the films were held between two graphite plates in order to reduce wrinkling. The untreated PVDF films were also heat-treated under the same conditions by placing them on a glassy carbon plate in order to avoid adhesion of the products to the substrate.

The carbonized fibers and films were activated using carbon dioxide gas. First, the specimens were heated at a heating rate of 10°C min^{-1} up to 850°C under nitrogen gas flow. Then, the flowing gas was changed to carbon dioxide and the specimen was activated at 850°C for a desired duration. The flowing gas was changed back to nitrogen, and the specimen was left to cool in the furnace down to room temperature. The flow rate of both nitrogen and carbon dioxide gasses was 500 cm^3 min^{-1}. The duration of activation was determined so that the mass loss during activation relative to the carbonized PVDF ($\Delta M_{act}/M_{heat}$) reached about 70% for all the specimens.

The pores developed in the carbon fibers and films were characterized with small-angle X-ray scattering (SAXS) by using a diffractometer (Rigaku), the PSPC and pinhole-collimated CuKα radiation. Specimens were prepared by aligning the carbon fibers and stacking the carbon films. The specimen-to-detector distance was 360mm and a height-limiting slit with 0.43 mm gap was attached at the X-ray entrance of the PSPC. Since SAXS of the pores in the PVDF-based carbon fibers and films was isotropic, it was possible to convert the SAXS profiles into those obtainable with an infinitely-long-slit collimation of the incident X-ray beam. From the converted profiles, the radius of gyration (R_3) of the pores was estimated according to a method proposed by the present authors [5,6]. If the pores are of spherical shape, their diameter D is given by (28/3)1/2 R_3. If the pores are of cylindrical shape, aligned in parallel to each other, and R_3 is estimated with this analysis method from the equatorial intensity distribution of the cylinders, their diameter D is given by 81/2 R_3.

The nitrogen gas adsorption-desorption isotherm was measured at 77K using an automatic gas adsorption apparatus (Autosorb-1, Quantachrome). From the isotherms measured, BET surface area, total pore volume and average pore diameter were calculated. Pore size distribution was determined from the desorption isotherm by applying the Barrett-Joyner-Halenda method to the desorption isotherm [7].

Adsorptive properties against methylene blue (MB) adsorbate which is accessible to the pores with diameters larger than 1.5 nm [8] was measured. The MB dye used showed 13.0% mass loss when heated at 135°C for 12 h under reduced pressure due to evaporation of water. By taking into account the degree of hydration of MB, aqueous solutions of MB with various concentrations in a range of 25-500 g m^{-3} were prepared. The carbon specimen of about 10 mg, dried at 135°C for 12 h under reduced pressure, was mixed with the solution of MB of 10 cm^3 in a test tube and shaken at 30°C for 24 h. The concentration of MB in the solution sampled by using a hypodermic syringe was measured. The adsorption of MB per unit mass of the specimen was calculated from the difference in the concentrations of MB in the solution before and after the specimen was added to the solution. The concentration of MB was determined by measuring the optical absorbance of the solution with a visible spectrometer (UV-2200, Shimazu) and using a calibration curve which had been constructed based on Beer's law.

3. RESULTS AND DISCUSSION

3.1. Dehydrofluorinated fibers and films

As dehydrofluorination progresses, the color of PVDF fibers and films was turned from white into black initially at the surface of the materials and eventually over the entire cross section. From the masses of the specimen before and after dehydrofluorination, the

mass loss during dehydrofluorination relative to the mass of the starting PVDF ($\Delta M_{chem}/M_{PVDF}$) was calculated. With increasing dehydrofluorination time, the $\Delta M_{chem}/M_{PVDF}$ value decreases and at a dehydrofluorination time of 12 h, these values reached 16 and 13%, respectively, for the fibers and films [4]. With the increase of $\Delta M_{chem}/M_{PVDF}$, the fluorine content decreased and the carbon content increased almost linearly [4]. Thus, $\Delta M_{chem}/M_{PVDF}$ will be used as the measure of the degree of dehydrofluorination.

3.2. Heat-treated fibers and films

During heat-treatment, untreated PVDF melted and only granular carbon was derived. On the contrary, dehydrofluorinated PVDF maintained its macroscopic precursor geometry during heat-treatment even though $\Delta M_{chem}/M_{PVDF}$ was as small as 2%. As a result, carbon fibers and films could be obtained without causing wrinkling and/or fragmentation. It is considered that multiple C-C bonds were introduced into the PVDF molecules by dehydrofluorination, which prevented fusion of PVDF during high-temperature heat-treatment.

During heat-treatment, rapid decomposition took place in the temperature range of 300-400°C, and the pores were formed in this temperature range. The change of the pore size with increasing heat-treatment temperature above 400°C was small.

The R_3 values of the pores in PVDF-based carbon fibers and films carbonized at 1300°C are plotted against $\Delta M_{chem}/M_{PVDF}$ in Fig. 1. For comparison, R_3 values of the pitch-, polyacrylonitrile- and phenol-based carbon fibers prepared in our laboratory at the carbonization temperature of about 1300°C were 1.2, 0.8 and 0.9 nm, respectively. In these cases, R_3 values represent the size of the pore cross section perpendicular to the fiber axis. For the commercial activated carbon granule derived from palm shells, R_3 value was 2.1 nm. By applying a slight dehydrofluorination, the pore size of the PVDF-based carbon increases as compared with that of the carbon derived from untreated PVDF. By applying an intensive dehydrofluorination, on the other hand, the pore size decreases. Thus, the pore size of the PVDF-based carbon can be controlled in a range of 0.3-2.3 nm by changing the degree of dehydrofluorination.

From the nitrogen gas adsorption, it was obtained that the PVDF-based carbon granule derived from untreated PVDF by heat-treatment at 1300°C had BET surface area of 761 $m^2\ g^{-1}$, total pore volume of 0.46 ml g^{-1} and average pore diameter of 2.41 nm. On the other hand, the PVDF-based carbon prepared by dehydrofluorination to a $\Delta M_{chem}/M_{PVDF}$ value of 7% and heat-treatment at 1300°C did not adsorb detectable amount of nitrogen gas. Thus, the pores detected with SAXS have closed structure. In order to make the pores in PVDF-based carbons accessible with adsorbate, activation was carried out.

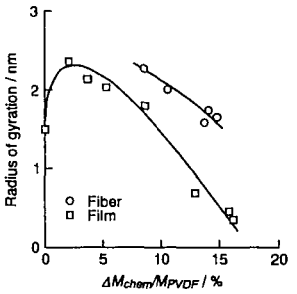

Fig. 1 Radius of gyration (R_3) of pores in PVDF-based carbon fibers and films versus $\Delta M_{chem}/M_{PVDF}$. Heat-treatment temperature was 1300°C. At the value of $\Delta M_{chem}/M_{PVDF}$ of 0%, film was pulverized during heat-treatment.

3.3. Activated carbon fibers and films

In the nitrogen gas adsorption-desorption isotherms of PVDF-based activated carbon films shown in Fig. 2, a steep increase of the amount of adsorption is found at low relative pressure region. This indicates that micropores are developed in the PVDF-based activated

carbons. For the activated carbon films which were prepared by applying dehydrofluorination to a $\Delta M_{chem}/M_{PVDF}$ value of 2%, the isotherm has a large hysteresis loop indicating the existence of mesopores. The hysteresis loop gradually diminishes and disappears at $\Delta M_{chem}/M_{PVDF}$ of 13%.

Pore size distributions of PVDF-based activated carbon films are shown in Fig. 3. Mesopores with a diameter of 2-4 nm are developed even though dehydrofluorination is not applied. In this case, however, the material is granular. By applying dehydrofluorination to a $\Delta M_{chem}/M_{PVDF}$ value of 2%, noticeable amount of mesopores with a diameter of 4-8 nm are formed. Intensive dehydrofluorination decreases the amount of mesopores.

As shown in Fig. 4, the average pore diameter, determined by nitrogen gas desorption, of PVDF-based activated carbon films is almost in proportion to the R_3 value determined by SAXS for the carbon films before activation. Therefore, the pore structure of the PVDF-based activated carbon films reflected that of the carbon films before activation.

Adsorption of MB, at equilibrium concentration of 3.0×10^{-4} mol l^{-1}, on PVDF-based activated carbon fibers and films are plotted against $\Delta M_{chem}/M_{PVDF}$ in Fig. 5. For comparison, the MB adsorption properties of various activated carbon granules cited from literature [2] are shown in Table 1. PVDF-based activated carbons exhibit superior adsorptive properties against MB. With appropriate preparation conditions, MB adsorption of 1.7×10^{-3} mol g^{-1} was achieved.

4. SUMMARY

By using a combination of chemical dehydrofluorination and high temperature heat-treatment, the PVDF-based activated carbon fibers and films were highly mesoporous and showed superior adsorptive properties against MB.

The advantage of PVDF-based activated carbon prepared in the present study is that it dose not contain impurity such as metal particles. This will be preferable for the application of activated carbons to catalyst supports or electrodes of electric double-layer capacitor.

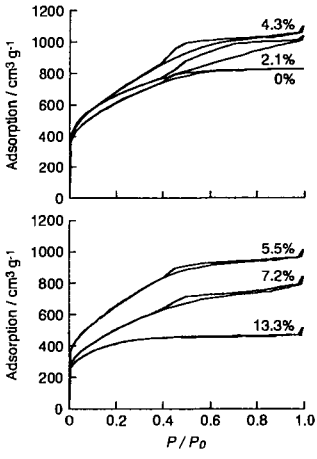

Fig. 2 Nitrogen gas adsorption-desorption isotherms at 77K, of PVDF based activated carbon films. The value of $\Delta M_{act}/M_{heat}$ was about 70% for all specimens. Values of $\Delta M_{chem}/M_{PVDF}$ are shown in the figure. At the value of $\Delta M_{chem}/M_{PVDF}$ of 0%, film was pulverized during heat-treatment.

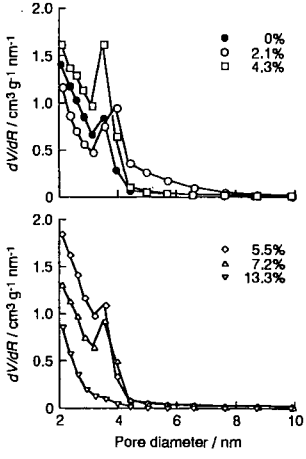

Fig. 3 Pore size distributions of PVDF based activated carbon films. The value of $\Delta M_{act}/M_{heat}$ was about 70% for all specimens. Values of $\Delta M_{chem}/M_{PVDF}$ are shown in the figure. At the value of $\Delta M_{chem}/M_{PVDF}$ of 0%, film was pulverized during heat-treatment.

Furthermore, the pore size is controllable in a wide range by changing the degree of dehydrofluorination. The good processability of PVDF into various geometries is also advantageous for applications.

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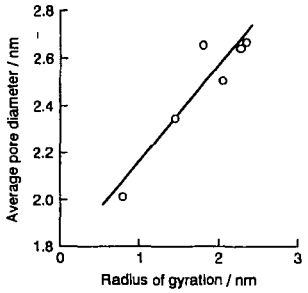

Fig. 4 Average pore diameter of PVDF based activated carbon films versus radius of gyration of PVDF based carbon films before activation. $\Delta M_{act}/M_{heat}$ was about 70% for all specimens. At the value of $\Delta M_{chem}/M_{PVDF}$ of 0%, film was pulverized during heat-treatment.

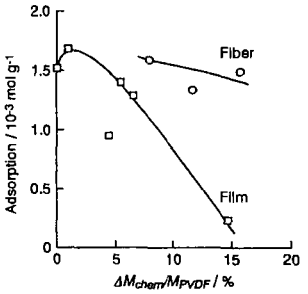

Fig. 5 Adsorption of methylene blue at equilibrium concentration of 3.0×10^{-4} mol l^{-1} at 30°C, on PVDF based activated carbon fibers and films versus $\Delta M_{chem}/M_{PVDF}$. The value of $\Delta M_{act}/M_{heat}$ was about 70% for all specimens. At the value of $\Delta M_{chem}/M_{PVDF}$ of 0%, film was pulverized during heat-treatment.

Table 1 Adsorption of methylene blue on various granular activated carbons.

Precursor	Adsorption / 10^{-3} mol g^{-1}
Palm shell	0.12
Coconut husk	0.20*
Bituminous coal	0.55*
Pitch	0.10*
Pitch/Y(naphthoate)$_3$	0.15*
Pitch/Y(OiPr)$_3$	0.16*

*Values were cited from reference [2].